AFCRL-62-87

APPLICATIONS OF TUNNELING TO ACTIVE DIODES

General Electric Company
General Electric Research Laboratory
Schenectady, New York

Scientific Report No. 7A

AF 19(604)-6623

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ELECTRONICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
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APPLICATIONS OF TUNNELING TO ACTIVE DIODES

Abstract

Calculated curves are given showing the solubilities of substitutional and interstitial Cu in GaAs in the presence of given amounts of donor and acceptor impurities as a function of temperature.

The solubility of Cu has been measured in pure and extrinsic p-type GaAs, Ge, and Si, and the results give the solubilities of the substitutional and interstitial species separately. The solubility ratios of these species in intrinsic GaAs, Ge, and Si at 600°C are approximately 30, 6, and 8 respectively.

The interstitial diffusion coefficients at 600°C are 3, 12, and $1.7 \times 10^{-5} cm^2/sec$ respectively, that of GaAs being given by $D_i = 0.03 \exp(-0.52ev/kT)$. In Si, the activation energy is nearly the same. A formula is given for the effective diffusion coefficient in intrinsic and extrinsic n-type semiconductor. In extrinsic n-type material the time constant for out-diffusion can be much greater than for in-diffusion.

Curves giving the intrinsic carrier concentrations at high temperatures in Ge, Si, and various 3-5 compounds are given.

An elementary theory of the liquidus curve in 3-5 compound phase diagrams is derived and compared with experiment. New data for GaP solubility in Ga are given which are much lower than that reported elsewhere.

The mean free paths of hot electrons in K, Al, and Au as a function of energy are calculated using the theories developed by Wolff and Quinn. Serious discrepancies between these calculations and some recent experimental values are discussed.

APPLICATIONS OF TUNNELING TO ACTIVE DIODES

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A. Calculation of the Solubilities of Substitutional and Interstitial Cu in GaAs

1. Review of Nomenclature and Assumptions

Experiments described in previous quarterly reports have shown that interstitial Cu has a high solubility in extrinsic p-type GaAs. From these measurements and those of Fuller and Whelan[1] of the combined solubility of substitutional and interstitial Cu in undoped GaAs it is possible to calculate the solubilities of both species of Cu in both n- and p-type material, thereby extending our knowledge of the behavior of Cu into regions that are not conveniently accessible experimentally, but which may be of considerable technological importance. For example, the heavily doped regrowth regions formed by alloying techniques exhibit greatly enchanced solubilities for Cu and can therefore serve as sinks or sources of Cu during subsequent stages of device fabrication.

The method of analysis was presented in report 6A, to which the reader is referred. The nomenclature which we use is repeated below:

C_s conc. of charged substitutional Cu.

C_{si} " " " " " in intrinsic GaAs.

C_{su} " " " " " " undoped " .

C_s^o " " neutral " " .

C_i " " charged interstitial Cu.

C_{ii} " " " " " in intrinsic GaAs.

C_{iu} " " " " " " undoped " .

N excess donor concentration (negative if p-type).

n free electron concentration.

n_i intrinsic carrier concentration.

Figure 1 shows the temperature dependence of the basic solubility parameters used in this analysis. C_{ii} was deduced from the enhanced interstitial solubility observed in p-type GaAs, as discussed below in Section B-2. C_{su} represents the data of Fuller and Whelan,[1] measured above 700°C. C_{si} was computed from their results in the same temperature region, and a straight line fit was made and extended to lower temperatures, and used to compute the rest of the C_{su} curve in this lower temperature region. The slight curvature of the C_{su} and C_{iu} curves is due to the fact that GaAs becomes increasingly extrinsic at higher temperatures when saturated with Cu, and the solubilities are affected accordingly. The solubility of neutral substitutional Cu, C_s^o, which is independent of the donor or acceptor doping, is also computed from the C_{si} curve.

Figure 1 also shows the intrinsic carrier concentration. This curve takes into account the two-band properties of the GaAs conduction band, as discussed in Section C of this report.

Two further assumptions were made in performing the solubility calculation:

a) It was assumed that substitutional Cu is a single acceptor, with a level 0.14 ev above the valence band edge, in spite of the fact that our measurements have shown that it is really a double acceptor, as described in Section B-7. This assumption was made to simplify the analysis, and because the position of the second level in the energy gap is not known. However it means that our analysis will underestimate the effects of donor and acceptor impurities upon the solubility of the substitutional species.

b) Ion pairing is neglected. Our experimental results indicate that pairing does not occur to an appreciable extent between either species of Cu and column 2 acceptor or column 4 donor impurities. However, there is evidence that substitutional Cu forms pairs with the column 6 donors.[2]

2. Results of Solubility Calculations

In this section we present the results of our calculations of the solubilities of interstitial and substitutional Cu in extrinsic GaAs. In discussing them, it is well to keep in mind

the qualitative aspects of the effect of shallow-level donor and acceptor impurities upon the solubility of the particular impurity under discussion. These may be summarized as follows:

a) If this impurity is a donor, its solubility will always be enhanced by the addition of shallow acceptors, and depressed by the addition of donors. The opposite holds true if the impurity is an acceptor.

b) The degree of enhancement or depression depends upon the factor by which the electron concentration is altered by the added donors or acceptors. It is proportional to the n-th power of this factor for an impurity carrying n units of electron charge.

c) If the solubility of the impurity under discussion is large compared with n_i in the undoped semiconductor, it will be enhanced by an opposite type shallow donor or acceptor which is present in even larger concentration until the semiconductor is almost exactly compensated. However, if the solubility in the undoped semiconductor is less than n_i, this close compensation will not generally occur.

From Figure 1 it is seen that $C_{su} > n_i$ above 600°C but becomes smaller than n_i at lower temperatures. Thus, according to c above, close compensation due to substitutional Cu is to be expected in heavily doped n-type material at high temperatures, but below 600°C only a small fraction of the donors will be compensated. This behavior is born out by the calculated curves of the solubility of

negatively charged substitutional Cu in GaAs, which are shown in Fig. 2. It will be recalled that these curves are calculated under the assumption that substitutional Cu is a single acceptor. Since we believe that it gives rise to two acceptor levels, it is expected that the solubility enhancement in n-type material is much greater than indicated by these curves, and that close compensation may be expected at temperatures well below 600°C. That fraction of the substitutional Cu which is electrically neutral is not included in these curves.

Figure 3 shows the corresponding curves for interstitial Cu. In strongly extrinsic p-type GaAs, where pronounced solubility enhancement of this species occurs, the solubility is given to a good approximation by the formula

$$C_i = C_{ii} N_A/n_i \ . \qquad (1)$$

The fact that the curves are not quite horizontal in this region is due to the variation of the ratio C_{ii}/n_i with temperature which may be seen in Fig. 1.

Figure 4 shows the total Cu solubility in p-type GaAs obtained by adding the results shown in the preceding diagrams. This is what is measured using radioactive Cu, and accordingly these curves are to be compared with the data shown in Fig. 1 of report 6A.

Cu diffusion may be used to reduce the carrier concentration in n-type GaAs, as reported by Blanc, et. al.[3] In this case it

is the net donor concentration, $N_D - C_s + C_i$, which is of interest. This quantity is plotted in Fig. 5. Conversion from n-type to p-type is expected to require saturation at 570°C for material containing 10^{16} cm^{-3} donors, and correspondingly higher temperatures for more strongly n-type specimens. Here, again, the fact that substitutional Cu is really a double acceptor means that conversion should occur at temperatures somewhat below those indicated by these curves. This is consistent with the findings of Blanc, et al.[3] The calculations shown in Fig. 5 are equivalent to their Fig. 16, except that we use slightly different values for C_{su}. We also take into account formally the presence of the interstitial Cu, although it has a neglegible effect upon these curves.

We believe that the inability to convert GaAs containing over 10^{18} cm^{-3} donors or to produce acceptor concentrations approaching the chemical solubility by high temperature Cu diffusion can be explained adequately by the rapid precipitation of Cu at these high temperatures. Even the most rapid quench rates that have been used in studying this phenomenon[3,4] are unable to prevent substantially complete precipitation and consequently the range of quenching rates that have been explored have not resulted in large differences in the amount of Cu remaining in solution. Similar problems have been encountered with the precipitation of Cu, Fe, and Li in Si,[5,6] and with Li in Ge.[7]

B. Experimental Measurements of the Properties of Substitutional and Interstitial Cu in GaAs, GaSb, Ge, and Si.

1. Solubility Measurements

Measurements of the solubility of Cu in intrinsic and in extrinsic n- and p-type GaAs using radioactive Cu have been described in previous reports. The importance of the two species of Cu in Ge and Si has been known for some time, but little quantitative information has been obtained regarding their relative abundances and diffusivities. In view of the success which we have had in studying this problem in GaAs, it seemed worthwhile to extend these same measurements to some of the other related semiconductors which are of current technological importance.

We were particularly interested in the possibility of confirming the very large solubility enhancement predicted by Shockley and Moll[8] for Cu in Ge. Actually, this enhancement is considerably smaller than they indicate because of failure to take into account the very large decrease in energy gap at high temperatures and because the value of n_i which they used was too small by a factor of five. Nevertheless, the effects are quite measurable, as will be described below.

In most cases, samples of the various semiconductors being studied were electroplated with Cu^{64} and heated in H_2 for times calculated from previous experience to be sufficient to saturate

the sample, and they were then cooled rapidly to room temperature. The gamma ray activity was measured at this point, and again after soaking in a KCN solution for a few minutes followed by a light chemical polish, to verify that a large excess of Cu was still on the surface at the end of the saturation period. The samples were then etched again more heavily, so as to remove about 10°/o of the weight, and a third count was made to obtain evidence that surface Cu was completely removed and that a uniform volume distribution of Cu was present. Some samples were given further etching and counting steps depending upon the results of these measurements. All of the samples were sectioned and contact radioautograms were made using heavy emulsion X-ray film. These negatives were of great value in detecting occasional inclusions of Cu which would have led to erronious results, and in determining whether the samples were uniformly saturated with Cu.

Densitometer measurements were also made on these negatives and each negative was calibrated by means of the gamma activity of those samples which were shown to be uniformly saturated. It was thus possible to determine the Cu solubility from the densitometer readings for those samples which contained non-uniform Cu distributions. These readings gave additional cross-checks upon the internal consistency of the various measurements which were made of the Cu concentration. The exposure density produced in an emulsion by a

given concentration of Cu (per unit volume) is inversely proportional to the stopping power of the semiconductor in which the Cu is dissolved for beta particles of the average energy emitted by Cu^{64}. The stopping power is approximately proportional to product of the number of atoms of each species per unit volume multiplied by their atomic number, and summed over each species in the host crystal. From this we conclude, and confirmed experimentally, that a given concentration of Cu in Ge, GaSb, and GaAs will produce nearly equal exposures, while in Si the exposure density will be 2.4 times greater.

We estimate the probable error associated with our determinations of the Cu concentration to be approximately 20°/o. The internal consistency of the several measurements made on each sample was usually better than 10°/o for samples that were seen to be of uniform composition from the radioautograms. A 4°/o tolerance is assigned by Oak Ridge to their determination of the activity of the Cu. Additional small errors arise from our calibration of the gamma ray counter which we used, and from a possible error in the 12.8 hr half-life reported for Cu^{64}. We have verified that the latter is not seriously in error and that the activity is not affected by any long-lived contaminants that might be present in small amounts and thus upset our calibrations.

2. Interstitial Cu Solubility in GaAs

Additional measurements have been made of the enhanced interstitial solubility of Cu in p-type GaAs. Figure 6 summarizes

all of our data by plotting C_{ii} calculated from Eq. (1) against temperature. Measurements on crystals containing a considerable range of Zn concentrations give the same values of C_{ii}, thus confirming the validity of Eq. (1). The straight line drawn through these points is given by,

$$C_{ii} = 1.6 \times 10^{21} \exp(-1.146 \text{ ev/kT}) \qquad (2)$$

This formula is a slight revision of the one given in report 6A, and takes into account the additional data accumulated since then.

Below 150°C the solubility data give values of C_{ii} which fall slightly higher than the straight line fit. This may be taken to indicate a real departure from linearity. However, in view of other evidence discussed below in section B-7 we feel that it is more likely due to the presence of some foreign contaminant (probably oxygen) in these crystals which pairs with the Cu, thereby enhancing the solubility somewhat.

3. Solubility of Cu in GaSb

Similar observations of the solubility of Cu in GaSb doped with varying amounts of Zn, Cd, and Ge were made. These measurements, which are of a preliminary nature, show the expected enhancement effects in strongly p-type material. They also show a very pronounced decrease in Cu solubility for intermediate acceptor concentrations, corresponding to the crossing-over of the curves in Fig. 4, which indicates an unusually large ratio of C_{si} to C_{ii}. These measurements will be given in more detail in the next report.

4. Interstitial Cu Solubility in Ge

Because of the large value of n_i compared with the interstitial Cu solubility in Ge, observations of enhanced solubility require heavily doped p-type crystals. Our experiments made use of crystals doped with Al and Ga in the range 1.6 to 40 x 10^{19} cm^{-3}, and saturation temperatures of 600 and 670°C. C_{ii} calculated from these data are plotted in Fig. 7, and compared with n_i and the data of Woodbury and Tyler.[9] The latter, being determined electrically, measures the difference between the substitutional and interstitial Cu concentrations. Our value for the ratio $\alpha = C_{si}/C_{ii}$ is in excellent agreement with that estimated by Tweet[10] from studies of diffusion and precipitation of Cu in Ge.

It should be noted that there is a discrepancy of a factor of 2.2 between our measurement of the total solubility ($C_{si} + C_{ii}$) in intrinsic Ge and that of Woodbury and Tyler which corresponds to $C_{si} - C_{ii}$. Our data point was determined from three wafers, having thicknesses varying from 0.7 to 1.5 mm, which were diffused together at 700°C for 25 hrs in H_2. Radioautograms of sections of these samples were not taken, but this diffusion time was 100 times that estimated to give saturation. Furthermore the samples gave solubilities agreeing within 5°/o of each other. Our only explanation for the discrepancy is that two strongly n-type samples (4 x $10^{19}$$cm^{-3}$ As) were also diffused with these undoped crystals, and they may have gettered all of the available Cu so that full saturation was not achieved. We plan to examine this discrepancy further.

5. Interstitial Cu Solubility in Si

Pronounced increases in interstitial solubility are readily observed in p-type Si. Preliminary data showing C_{ii} measured on a variety of samples are reported in Fig. 8. They show considerable scatter which we tentatively attribute to nonuniform impurity concentrations in the crystals used. In many cases such concentration gradients were evident from the radioautograms. Further experiments are planned with more carefully doped crystals.

Early measurements of total Cu solubility[11] using radioactive tracers showed a curious flattening-off of the solubility curve at 600°C as shown at A, Fig. 8, which is quite unexpected.[12] We have remeasured the total solubility of Cu in this lower temperature range using floating zone Si, and find a much smaller value at this temperature which is consistent with theoretical expectations, although at still lower temperatures the curve again appears to level off, as at B. Since oxygen is known to be present in such crystals in this general range of concentrations, we presume that the leveling-off is due to pairing of Cu with dissolved oxygen, thus giving an anomalously high solubility. A similar leveling-off of the solubility has been observed in GaAs, as discussed in section B-7.

We also conclude from Fig. 8 that in Si the ratio of the substitutional to interstitial solubilities, α, is approximately 8, a value considerably larger than that estimated from earlier

experiments.[13] Because of the large amount of scatter which exists among these preliminary results, this value for α may require revision.

6. Interstitial Diffusion in GaAs, Ge, and Si

The diffusion coefficient of interstitial Cu in GaAs has been measured between 100 and 600°C, and the method and results were given in report 6A. We have made similar measurements in Si, and find values only slightly smaller with nearly the same activation energy. These results are shown in Fig. 9. We also report a single measurement in Ge at 600°C, where $D_i = 1.2 \times 10^{-4}$ cm^2/sec. The dashed line drawn through this point has the same intercept at $1/T = 0$ as for Si, 0.008 cm^2/sec.

Some comments may be made regarding the "effective diffusion coefficient" of Cu in intrinsic and n-type semiconductors of this kind. Except in highly perfect crystals it may usually be assumed that local equilibrium exists between the substitutional and interstitial species, and consequently the dissociative diffusion process of Frank and Turnbull[14] applies. Under these circumstances Cu obeys the simple diffusion equation, with an effective diffusion coefficient in intrinsic material given by

$$D_{eff,int} = D_i/(1 + \alpha) \qquad (3)$$

In an extrinsic n-type sample the concentration of the interstitial species is decreased by the factor $n/n_i \approx N_D/n_i$, while that of the substitutional Cu will be increased by at least this large a factor.[8]

In a semiconductor where the substitutional Cu acquires r electron charges the increase may approach a factor of $(N_D/n_i)^r$. In Ge and Si r = 3, while in the 3-5 compounds r = 2. Therefore, in extrinsic n-type crystals, the effective diffusion coefficient is reduced still further,

$$D_{eff,ext} = D_i(n_i/N_D)^m(1 + \alpha)^{-1} \qquad (4)$$

where $2 < m < r+1$. It is to be noted that the diffusion coefficient can be expected to decrease very rapidly with increasing donor concentration and decreasing temperature.

Cu diffusion is thus expected to occur at a reduced rate in extrinsic n-type GaAs, and if the Cu concentration is small compared with that of the donor impurities, the penetration should still obey Fick's law. However, as shown by Fig. 5, the solubility enhancement may often be enough to reduce the free electron concentration by a substantial factor. This will cause a corresponding increase in the interstitial/substitutional ratio, and hence in the diffusion coefficient. The penetration profile in such a case will consist of a nearly uniform layer near the surface where the donors are closely compensated and D is large, followed by an abrupt concentration decrease where Fick's law diffusion takes place, with a much smaller diffusion coefficient. It is important to recognize that although Cu can be diffused <u>into</u> n-type GaAs to a considerable distance because of this nearly compensated layer, the

Cu cannot be removed again at the same temperature in a comparable time. As soon as the Cu is depleted to the point where the material is no longer closely compensated D drops to the value given by Eq. (4) rather than that characteristic of intrinsic GaAs, and consequently the out-diffusion process takes a correspondingly longer time.

7. Further Observations Regarding Cu in GaAs

Substitutional Cu has been shown to be a triple acceptor in Ge.[9] It is generally believed to be a single acceptor in the 2-6 compounds. In each case, this behavior is consistent with the valency of Cu, and it is reasonable to expect that substitutional Cu should behave as a double acceptor in the 3-5 compounds. Initial experiments, in which Cu was diffused into GaAs near 600°C, appeared to confirm these expectations.[1] However, from more recent experiments on Cu diffused into GaAs in the 1000 to 1200°C range it was concluded that Cu gave rise to only a single acceptor level.[15] The experiments described below confirm the double acceptor behavior of Cu near 600°C.

Samples were cut from neighboring regions of a single crystal of boat-grown n-type GaAs. Two were rectangular, 3.5 x 8 mm, with thicknesses 1/2 and 1 mm respectively. Contacts were applied to these two and their Hall coefficients were measured at 300°K, giving carrier concentrations of 8.0 and 8.2 x 10^{16} cm^{-3} respectively, assuming the formula $R = 3\pi/8$ en. The third was of irregular shape

with its minimum dimension approximately 3 mm, and it was presumed that it had a similar electron concentration, 8×10^{16} cm^{-3}. They were electroplated with Cu^{64} and diffused in H_2 for 46 hrs at 600°C. Following this diffusion treatment they were cooled to room temperature in less than 30 sec, and all were found to have gone high resistivity throughout. The gamma ray activity gave carrier concentrations of 5.0, 4.5, and 4.3×10^{16} cm^{-3} respectively. The loss in electrons per Cu atom is thus 1.60, 1.82, and 1.9 respectively. Since impurity scattering contributed substantially in these samples, it seems reasonable that the factor in the Hall coefficient formula should have been somewhat greater than the $3\pi/8$ value which was used. We conclude that Cu diffused into GaAs near 600°C introduces two acceptor levels which are located near or below the middle of the energy gap. Examination of published data[3,15] suggests that these may be located at approximately 0.14 and 0.42 ev above the valence band edge.

Fuller and Whelan have measured the solubility of Cu in undoped GaAs above 700°C. We have made similar measurements at lower temperature to look for departures from their extrapolated curve which might account for some of the large trap concentrations reported for samples diffused at these lower temperatures.[16] High impedance GaAs wafers were electroplated with Cu^{64} and diffused in H_2 for 3.4 hrs at 500°C and 24 hrs at 600°C. The 500°C wafers showed a Cu penetration which was 1/4 mm deep, with a concentration

estimated to be between 1.5 and 1.8 x 10^{16} cm^{-3}, which is over 10 times that obtained by extrapolation of Fuller and Whelan's data. On the other hand, the 600°C samples had concentrations of 1.4 x 10^{16} cm^{-3}, which fall close to their curve. The radioautograms of these samples showed that the distribution of Cu was "patchy," with variations of perhaps 30°/o occuring over a scale of one or two mm. This "flattening-off" of the solubility curve appears very similar to that found in Si as shown in Fig. 8, and it may well be due to a contaminant such as dissolved oxygen. It is also similar to the behavior noted in Fig. 6. As described in an earlier quarterly report[17] we have also found that not all of the Cu which is diffused into GaAs is removed by out-diffusion to a gettering agent. The amount left in the crystal is presumably paired with some impurity, which could easily be the same one that is responsible for the enhanced solubility.

C. Intrinsic Carrier Concentrations at High Temperatures

Calculations of solubility enhancement such as those described earlier in this report require a knowledge of the intrinsic carrier concentration at temperatures approaching the melting point of the semiconductor. Curves showing n_i as a function of temperature have been constructed for a number of semiconductors. Since these results may be of general interest they are reported here, with a discussion of the methods used in obtaining them.

In general, when only a single conduction and single valence band are involved, it is expected that n_i will have the form

$$n_i = AT^{3/2} \exp(-e E_{go}/kT) \qquad (5)$$

E_{go} is the value of the energy gap extrapolated to T = 0, and A involves the densities of states masses and a factor due to the temperature coefficient of the energy gap. The procedure adopted for the single conduction and valence band semiconductors was to fit the above formula to the highest temperature data published for n_i that appeared reliable in order to extend these data to higher temperature. Well established values for n_i and E_{go} are available for Ge and Si. Data for most of the 3-5 compounds was taken from recent literature.[18,19] In some cases the calculation of n_i required further elaboration:

GaSb - Leifer and Dunlap[20] give n_i data for temperatures up to 640°C, but they do not apply Sagar's two-band correction[21] to their Hall measurements. Furthermore the samples were sufficiently impure that the lower temperature data do not give reliable values for n_i. We therefore obtained a curve for n_i by assuming that all of the electrons are excited to the (111) conduction band which we assume is like that of Ge except 0.108 ev farther from the valence band. We thus multiplied the Ge curve by exp(-0.108/kT). This agrees within 20°/o with the 640° data of Leifer and Dunlap with

the two-band correction applied (a factor of 1.85), but below 400°C the agreement is poor. We attribute the poor agreement to the experimental difficulties mentioned above.

GaAs - A two-band correction similar to that used for GaSb is required at high temperatures in GaAs. The curve shown was calculated from the energy gaps and effective masses reported for this material using a density of states for the (100) band that is 100 times that of the (000) band as indicated by the temperature dependence of the Hall data.[19] The results agree well with the Hall measurements of Whelan and Wheatley,[22] with the two-band correction applied.

AlSb - Since the band structure of this material is apparently similar to that of Si,[19] and there are no other nearby band edges, we estimated n_i by correcting the Si curve for the difference in energy gaps as in the case of GaSb.

Figure 10 shows the results of these calculations.

D. Crystal Growth From Solution

1. Solubility of P, As, and Sb in Ga

We have frequently found it desirable to grow crystals of various 3-5 compounds from a solution consisting of an excess of one of the constituents, usually the column 3 element. In spite of the fact that similar experiments have been reported by a number of other workers, the appropriate regions of the phase diagrams

have not been well documented. We give below an elementary theory of the liquidus curve in such systems, and compare it with some experimental results.

It is generally known that the freezing point of a pure substance is lowered initially in proportion to the molar fraction of an impurity which is added to the system. If we assume negligible solubility in the solid phase, and that the solution is ideal, the liquidus curve is given by

$$T - T_m = \frac{RT}{\Delta S} \ln X \qquad (6)$$

where T_m is the melting point of the pure substance, X is the mole fraction of this substance in the solution, and ΔS is its entropy of fusion. R is the gas constant.

In the case of compound formation, it might be expected that a similar linear initial decrease in temperature would occur on either side of the solubility maximum corresponding to the composition of the compound. However, if the species which form the compound are dissociated in the liquid phase, as is expected for the 3-5 compounds, this does not occur, but instead the liquidus attains a horizontal slope near the compound composition.[23] A formula analogous to Eq. (6) which is applicable to the 3-5 compound phase diagrams in the temperature and composition range where the compound is in equilibrium with a liquid phase can be derived using

an argument similar to that given by Noyes and Sherrill[24] for the derivation of Eq. (6).

We start with their Eq. (40) in the form,

$$\frac{dT}{T^2} = \frac{R}{T_m \Delta S} \; d \ln p \tag{7}$$

From the derivation of this equation, we note that ΔS is the entropy of fusion per mole of the compound, and that p is the partial pressure of this same bimolecular species. The latter is proportional to the product of the concentrations of the two components of the system, X(1-X), again assuming that the solution is ideal and that there is no tendency toward compound formation in the liquid phase. Upon integration, we obtain the desired equation,

$$T - T_m = \frac{RT}{\Delta S} \ln[4 X \; (1-X)] \tag{8}$$

Kubaschewski and Evans[25] suggest rules for estimating entropies of fusion. ΔS is 6.0 and 6.6 cal/deg-gram-atom for Ge and Si, and 2.2 for typical metals. It is presumably somewhat less than 6 per atom (or 12 per molecule) for the 3-5 compounds, since these are closely related to Ge and Si. In Figure 11 we give curves for GaP, GaAs, and GaSb calculated from Eq. (8) assuming ΔS = 9 cal/deg-gram-mole and giving T_m the reported values.[18,26] Data for GaSb and GaAs taken from Hansen[27] are included, and show reasonable agreement with the calculated curves. Recent data for GaP[26] behave as expected

at high temperatures, but indicate an unexpectedly high solubility at 850°C. We report measurements of the solubility of GaP in Ga at 920 and 1100°C which are lower than the RCA data by at least a factor of 20 in this low temperature region. We are currently conducting measurements of the low temperature portion of the liquidus curve in these systems and in each case we find that the solubility is considerably smaller than that of the calculated curves. These results suggest that ΔS is closer to 12 cal/deg-gram-mole, and thus almost identical to that for Ge and Si on a per-atom basis.

2. Growth of GaP from Ga Solution

The magnetically stirred crystal grower described in the preceding report was operated several times, using charges of 100 grams of Ge, and temperatures between 1000 and 1100°C. GaP was grown, and it was observed that transport occurred as anticipated. Fluid rotation between 1/2 and 1 rps was clearly observed. Approximately 12 grams of polycrystalline GaP were produced per run. The smallness of the crystals produced is attributed to fluctuations in temperature due to the use of an unregulated RF heater supply, and to excessive thermal gradients. The equipment has been redesigned and operation in the near future is planned.

E. Calculations of Mean Free Paths of Hot Electrons in Metals

Further experiments have been reported which give evidence regarding the mean free paths of hot electrons in solids. However, the conclusions reached from these experiments are not easily reconciled with each other. From photoelectron emission studies in the alkali-antimonide

semiconductors[28] it was concluded that the pair production mean free path for electrons decreases from 100Å to 10Å as the energy is increased from a few tenths of a volt above threshold (roughtly 5 ev) to several volts above threshold. These values can reasonably be expected to serve as upper limits to the mean free paths of electrons of comparable energy in metals, where the electron population is greater and there is no energy threshold. However, much longer mean free paths are indicated by experiments with Au films, for electrons of 1 ev energy[29] as well as for those in the 7 to 10 ev range.[30]

Because of these and earlier experimental results which in some cases indicated very long mean free paths, it seemed instructive to perform calculations of hot electron mean free paths for some metals of particular interest, using the theory of Wolff[31] modified so as to apply to lower energy electrons,[32] as well as one recently developed by Quinn.[33] The latter gives the mean free path for an arbitrary loss in initial energy, whereas Wolff's theory considers collisions in which typically half of the initial energy is lost. In order to compare the results of these theories, calculations were made for K, Al, and Au, assuming collisions in which the final energy, E_f, was half of the original energy. The results, plotted against initial energy, are shown in Figs. 12 and 13. The parameters chosen to represent these metals are tabulated below:

Metal	Fermi Energy	Electron Concentration
K	2.04 ev	1.32×10^{22}
Au	5.55	5.93
Al	11.7	18.2

It is gratifying to note that in the regions where the theories are expected to be valid they indicate similar behavior and give quantitative agreement within a factor of two. Both predict much shorter mean free paths in Au than those indicated by the experiments mentioned above. (The experiments of Spitzer et. al. were concerned with electrons which lost less than about 20% of their initial energy, in which case the mean free path is some five times shorter than that given by Fig. 13). Thus a serious discrepancy still remains between the theoretical mean free paths of hot electrons and the results deduced from experiments using thin evaporated metal films. In such experiments the uniformity and freedom from defects of the films is of particular concern.

F. Plans for Further Study

It is expected that the studies of Cu solubility in semiconductors will be concluded during the next quarter.

The experiments on growth of crystals from solution will be continued.

Further studies will be made of the failure mechanism in GaAs tunnel diodes and its possible relation to Cu and other kinds of imperfections.

Plans are being made to conduct experiments relating to the problem of energy losses of electrons in metals and insulators.

RNH:erm
2/1/62

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FIGURE CAPTIONS

Fig. 1 Solubility parameters for substitutional and interstitial Cu in GaAs.

Fig. 2 Solubility of negatively charged substitutional Cu in GaAs. It is assumed that Cu is a single acceptor, 0.14 ev above the valence band.

Fig. 3 Solubility of positively charged interstitial Cu in GaAs.

Fig. 4 Total Cu solubility in p-type GaAs.

Fig. 5 Excess donor concentration remaining at room temperature after GaAs containing N_D shallow donors is saturated with Cu at temperatures indicated. Dashed curves indicate conversion to p-type.

Fig. 6 Solubility of interstitial Cu in intrinsic GaAs, C_{ii}, from experiments with extrinsic p-type samples. The departure from linearity at low temperature may be due to oxygen, see text.

Fig. 7 Solubility of interstitial Cu in intrinsic Ge, C_{ii}, from experiments with extrinsic p-type Ge. The intrinsic carrier concentration and the total Cu solubility, as determined by Woodbury and Tyler[9], are shown for comparison.

Fig. 8 Solubility of interstitial Cu in intrinsic Si, C_{ii}, from experiments with extrinsic p-type Si. The intrinsic carrier concentration and the total Cu solubility are shown for comparison. Departures from linearity at A and B are attributed to oxygen, see text.

Fig. 9 Interstitial diffusion coefficients measured in p-type Ge and Si, compared with similar data in GaAs presented in report 6A.

Fig. 10 Temperature dependence of intrinsic carrier concentrations in Ge, Si, and several 3-5 semiconductors.

Fig. 11 Theoretical and experimental liquidus curves for GaP, GaAs, and GaSb in Ga.

Fig. 12 Calculated mean free paths for electrons of initial energy $2E_f$ and final energy E_f, using Wolff's theory.

Fig. 13 Calculated mean free paths for electrons of initial energy $2E_f$ and final energy E_f, using Quinn's theory. The results are not expected to be accurate in the dashed region.

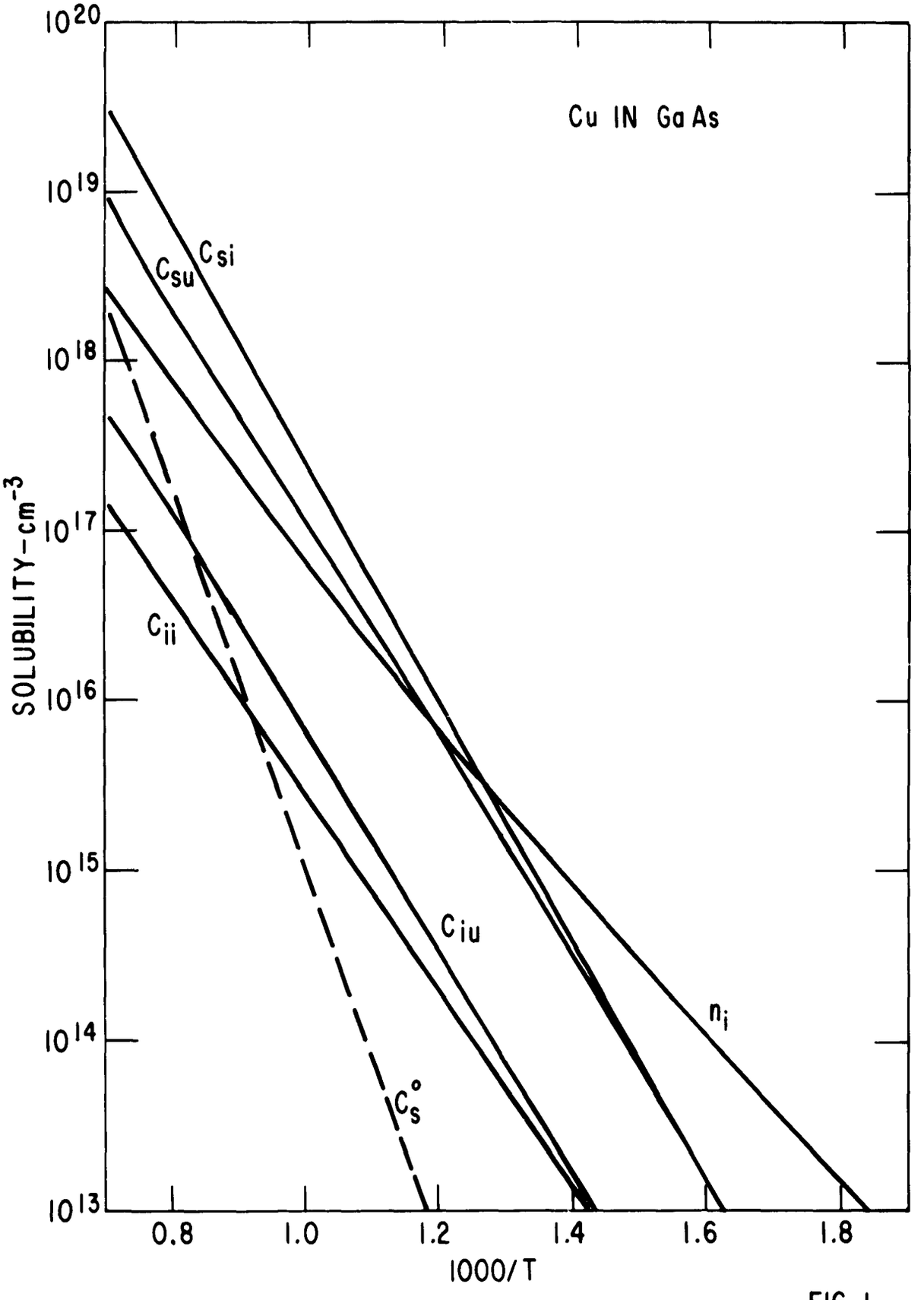
Cu IN GaAs
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
SOLUBILITY-cm^{-3}
C_{si}
C_{su}
C_{ii}
C_{iu}
n_i
C_s^o
0.8
1.0
1.2
1.4
1.6
1.8
1000/T

FIG. 1

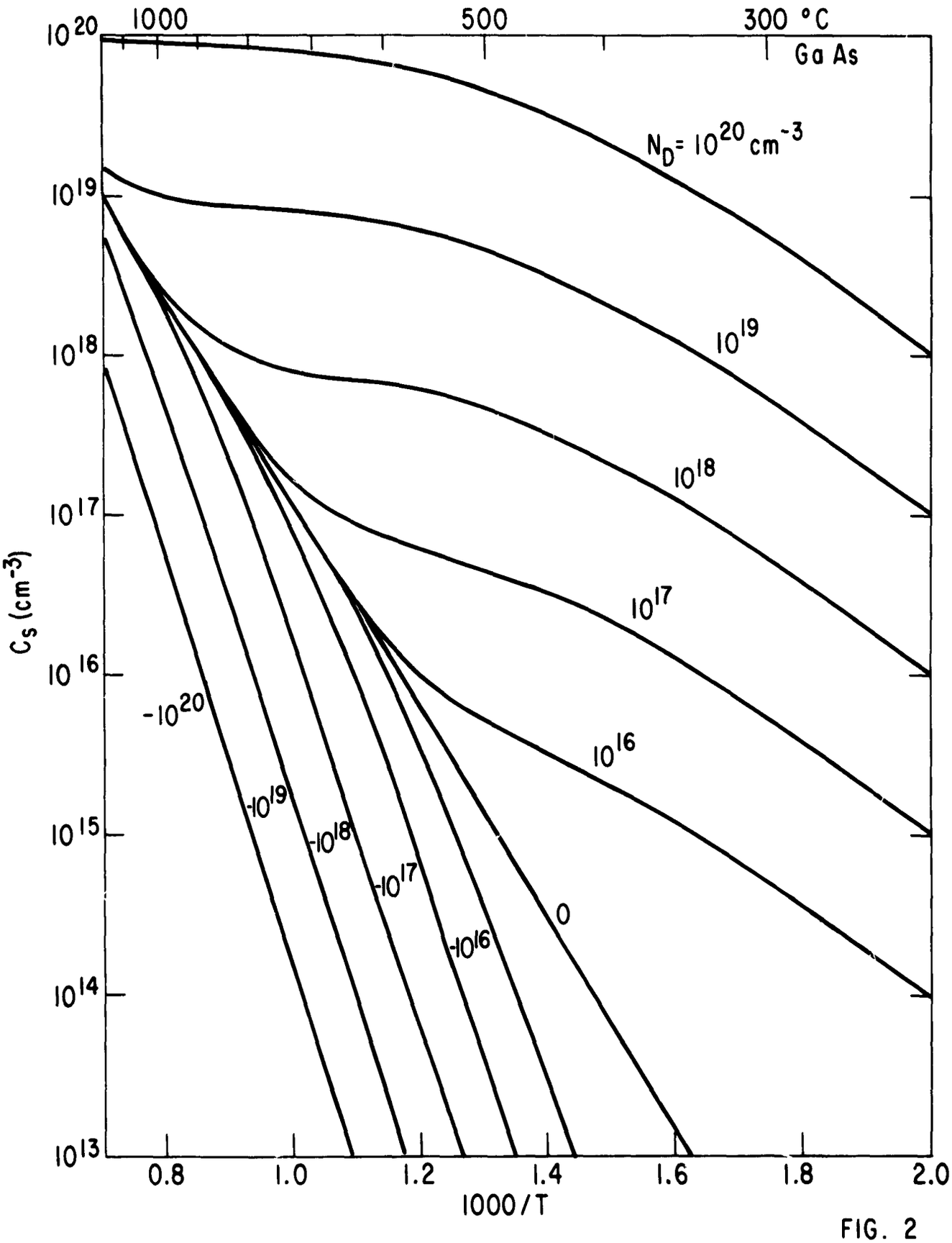
1000
500
300 °C
Ga As
$N_D = 10^{20}\,cm^{-3}$
10^{19}
10^{18}
10^{17}
10^{16}
-10^{20}
-10^{19}
-10^{18}
-10^{17}
-10^{16}
0
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
$C_S\,(cm^{-3})$
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1000/T

FIG. 2

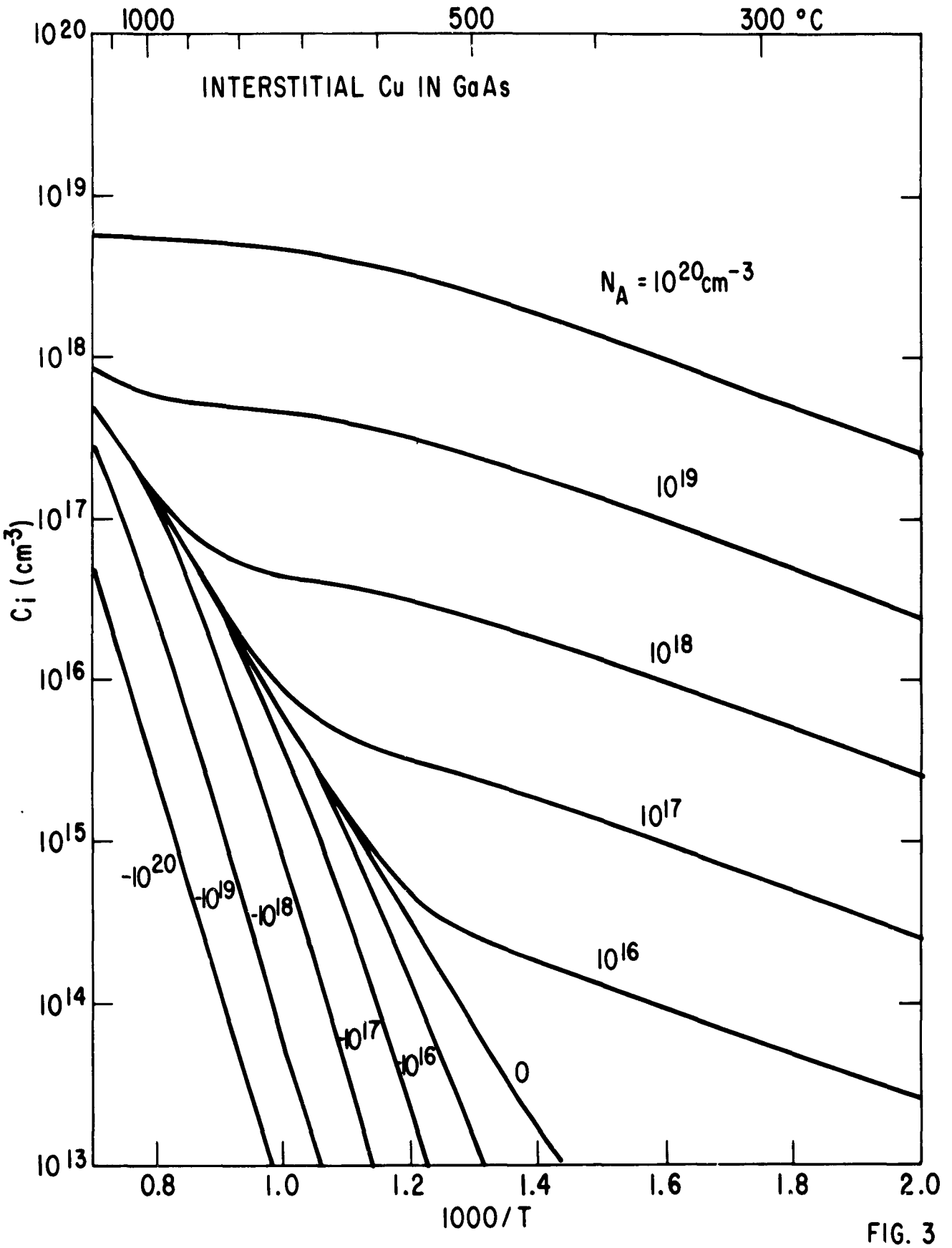
1000
500
300 °C
INTERSTITIAL Cu IN GaAs
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
C_i (cm^{-3})
$N_A = 10^{20} cm^{-3}$
10^{19}
10^{18}
10^{17}
10^{16}
0
10^{16}
10^{17}
10^{18}
10^{19}
10^{20}
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1000/T

FIG. 3

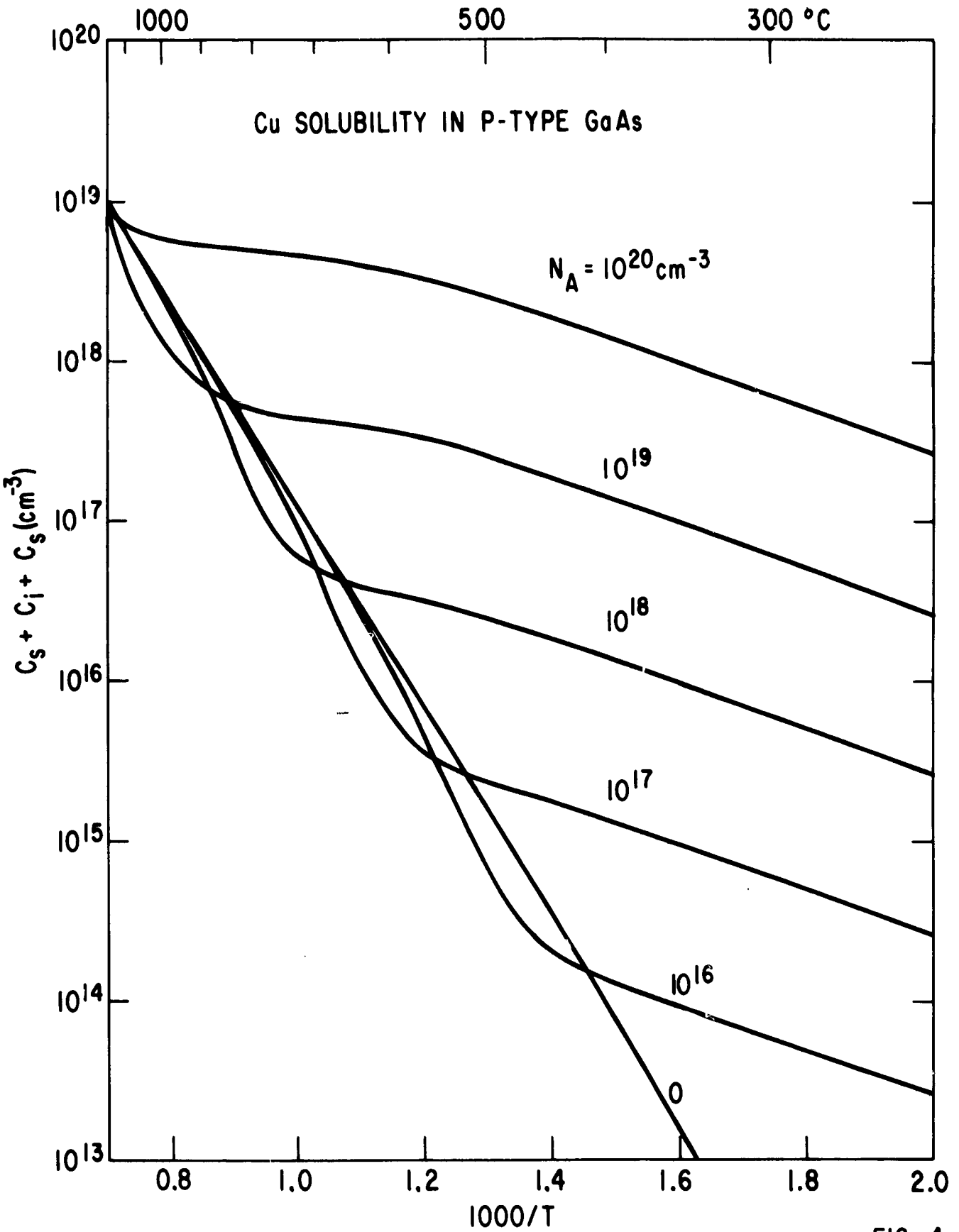
1000
500
300 °C
Cu SOLUBILITY IN P-TYPE GaAs
$N_A = 10^{20} cm^{-3}$
10^{19}
10^{18}
10^{17}
10^{16}
0
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
$C_s + C_i + C_s (cm^{-3})$
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1000/T

FIG. 4

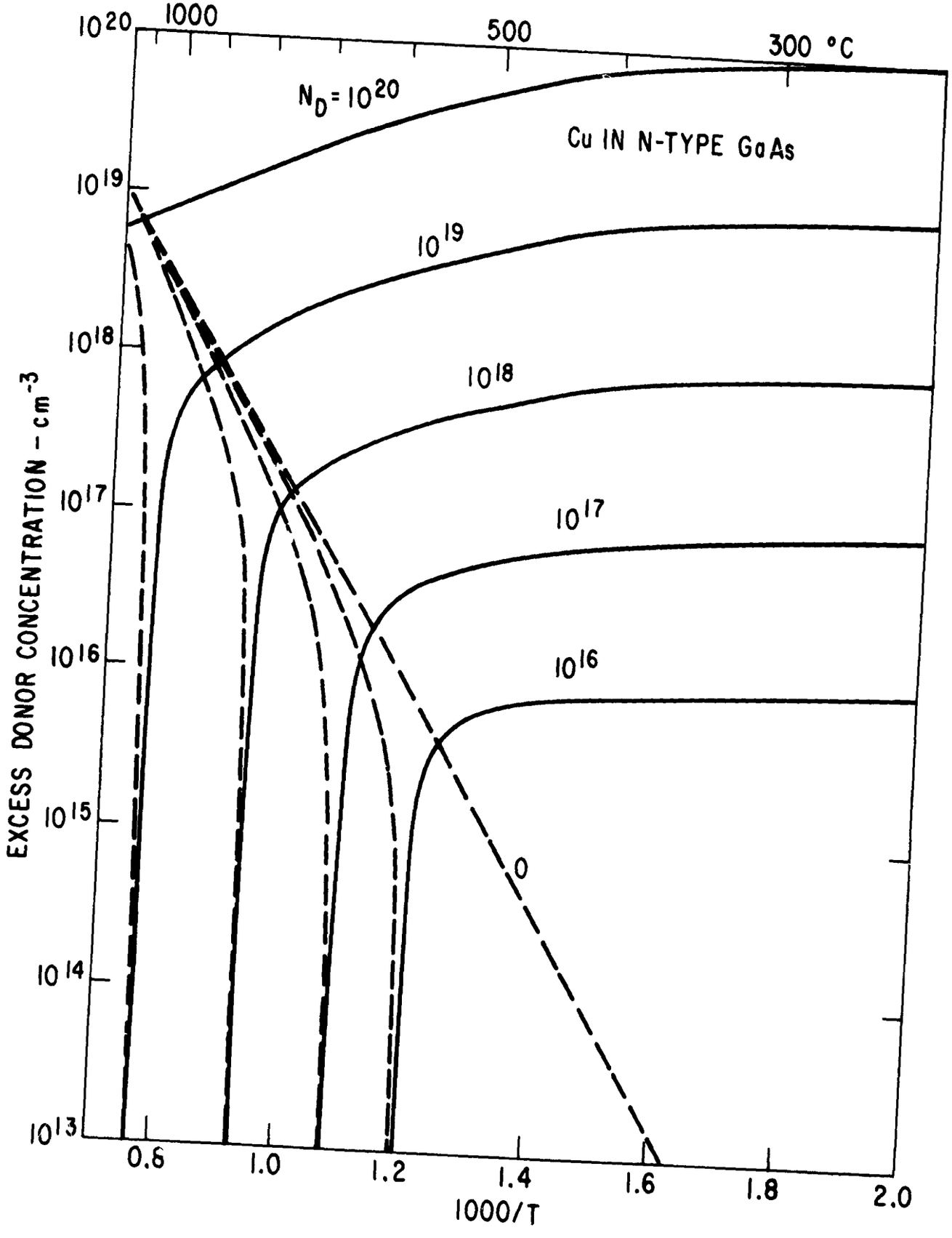
1000
500
300 °C
$N_D = 10^{20}$
Cu IN N-TYPE GaAs
10^{19}
10^{18}
10^{17}
10^{16}
0
EXCESS DONOR CONCENTRATION - cm^{-3}
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
0.6
1.0
1.2
1.4
1.6
1.8
2.0
1000/T

FIG. 5

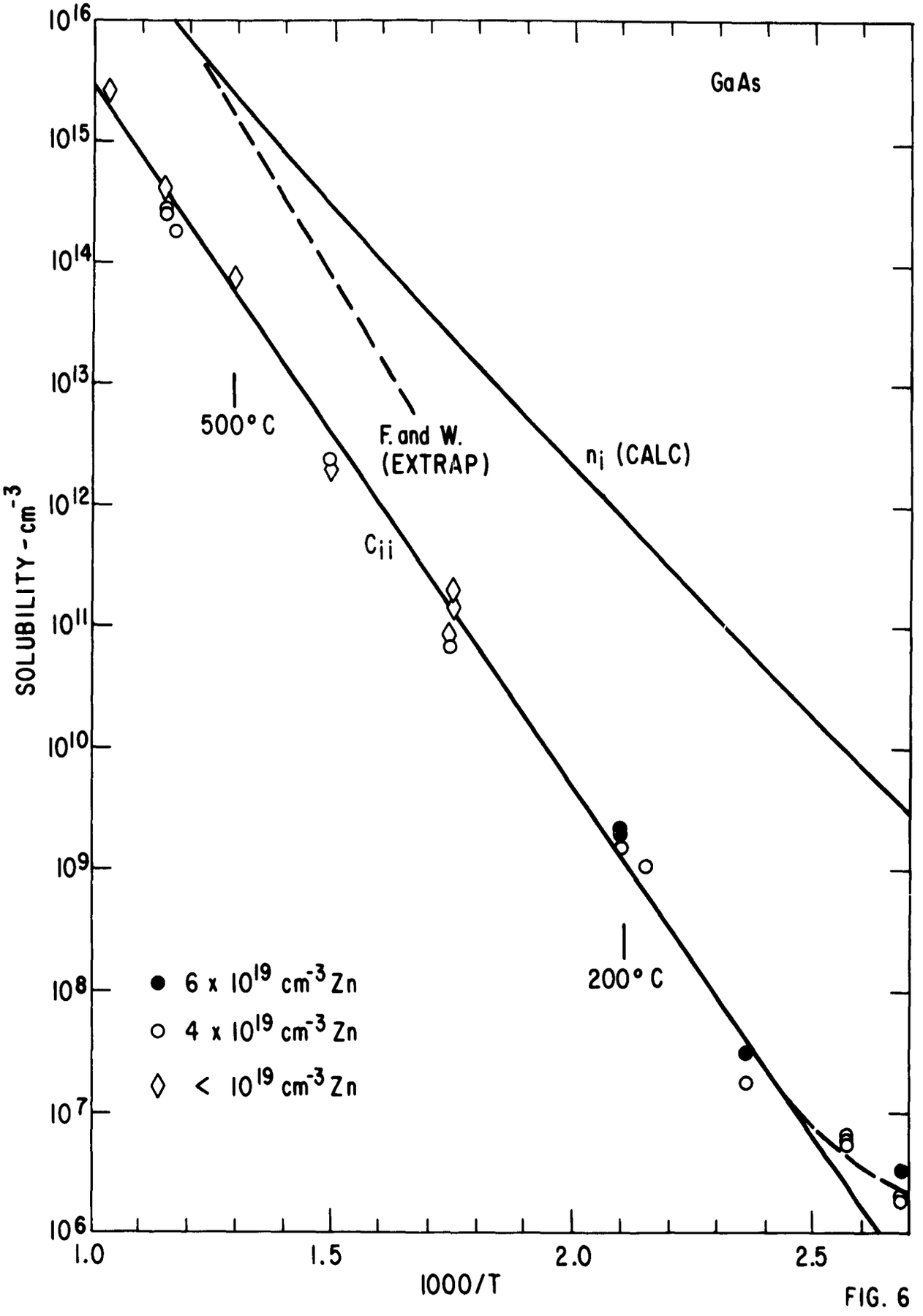
GaAs
SOLUBILITY - cm^{-3}
1000/T
500° C
200° C
F. and W.
(EXTRAP)
n_i (CALC)
C_{ii}
● 6 x 10^{19} cm^{-3} Zn
○ 4 x 10^{19} cm^{-3} Zn
◇ < 10^{19} cm^{-3} Zn
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
1.0
1.5
2.0
2.5

FIG. 6

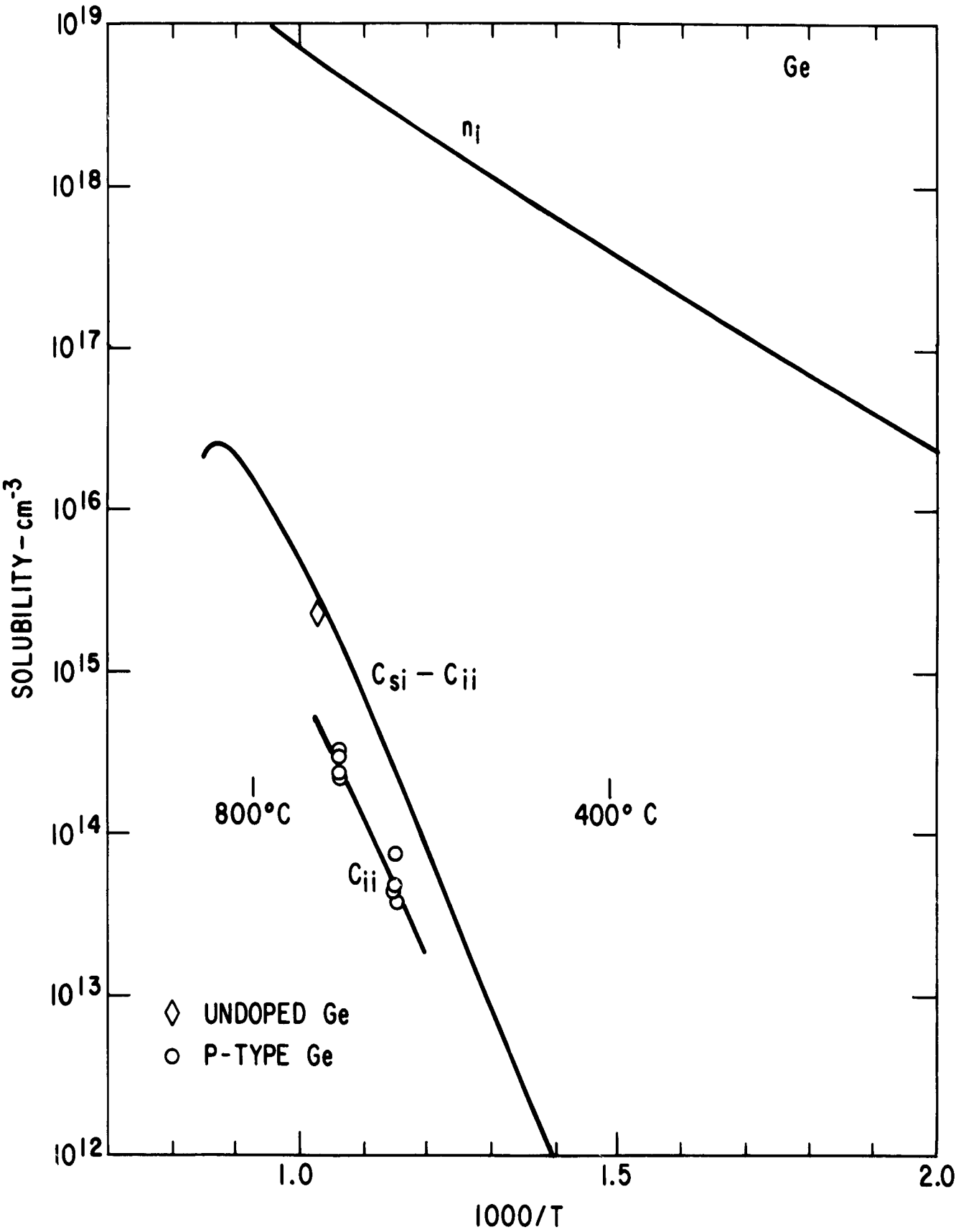
Ge
n_i
$C_{si} - C_{ii}$
C_{ii}
800°C
400° C
◇ UNDOPED Ge
○ P-TYPE Ge
SOLUBILITY-cm^{-3}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
1.0
1.5
2.0
1000/T

FIG. 7

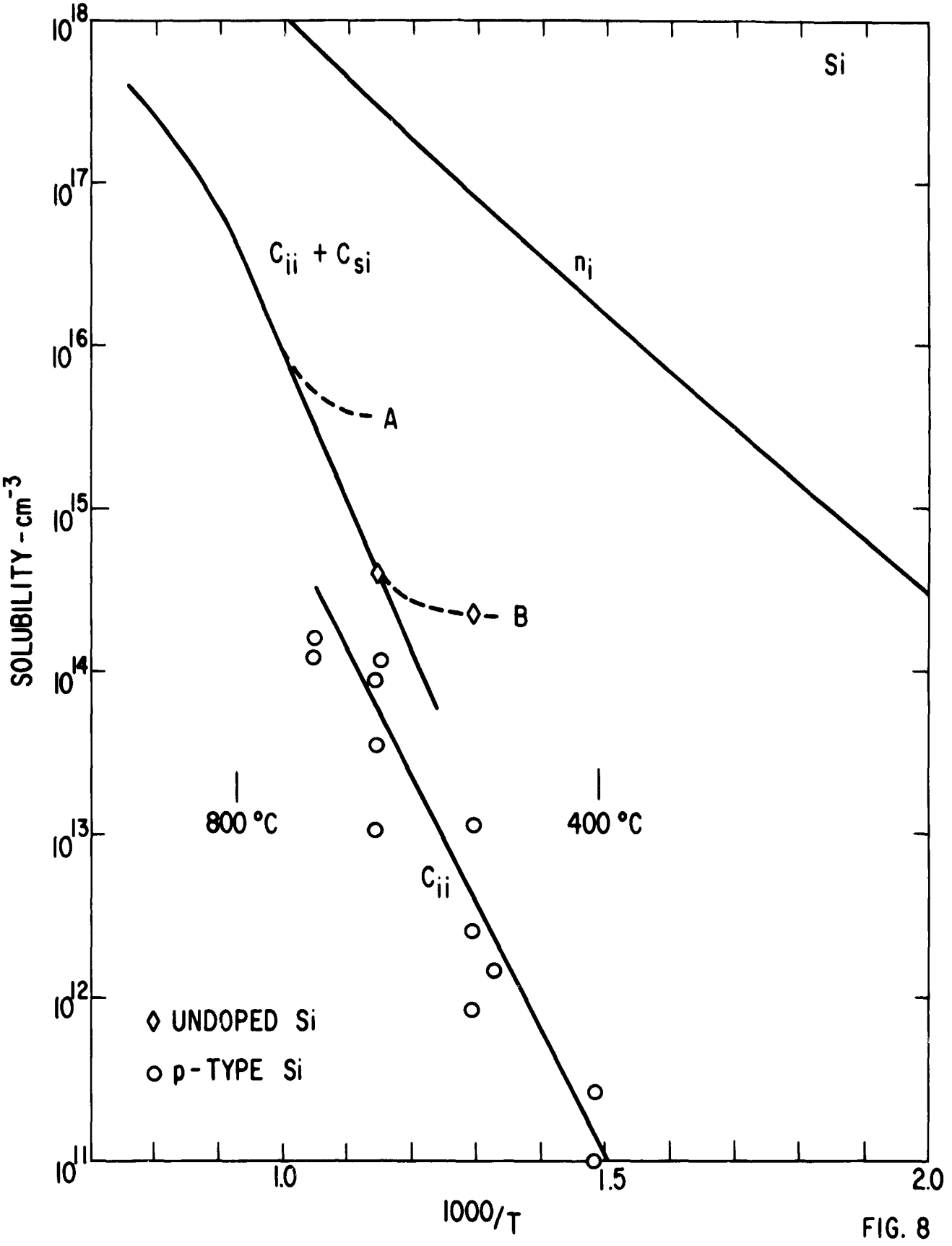
Si
$C_{ii} + C_{si}$
n_i
A
B
800 °C
400 °C
C_{ii}
◊ UNDOPED Si
o p-TYPE Si
SOLUBILITY - cm^{-3}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{12}
10^{11}
1.0
1.5
2.0
1000/T

FIG. 8

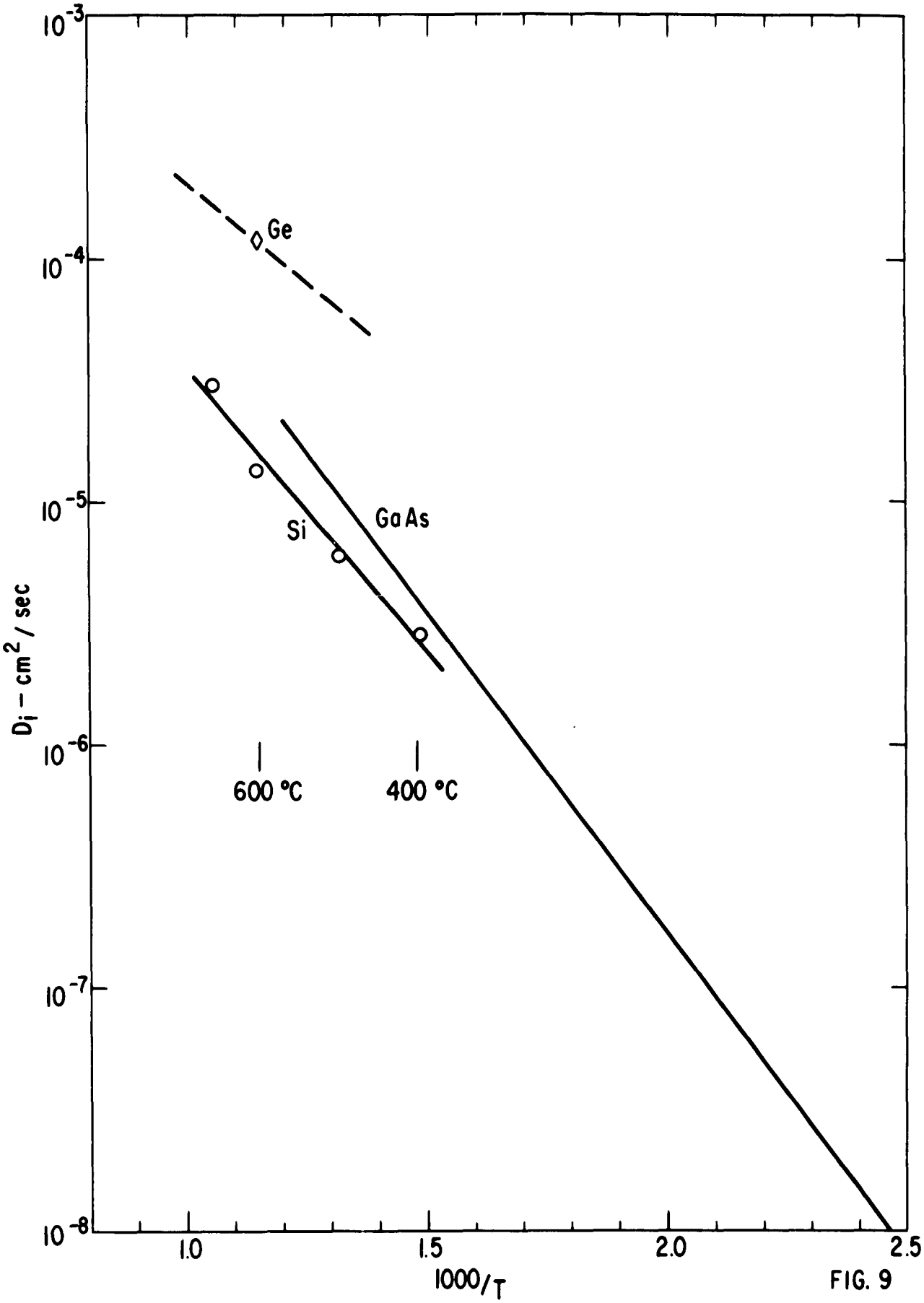
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
Ge
Si
GaAs
600 °C
400 °C
D_i – cm^2 / sec
1.0
1.5
2.0
2.5
1000/T

FIG. 9

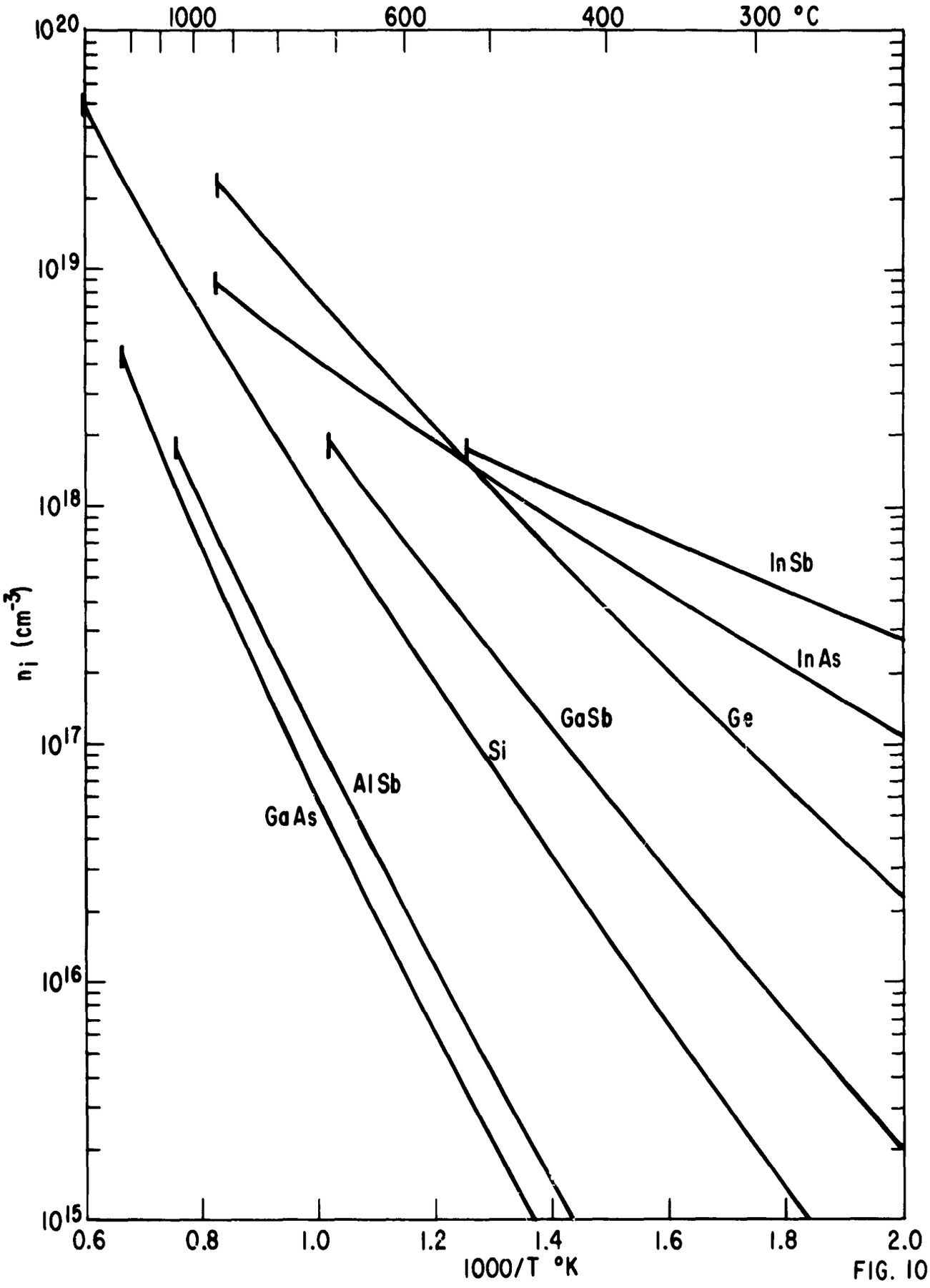
1000
600
400
300 °C
10^{20}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
n_i (cm^{-3})
InSb
InAs
GaSb
Ge
Si
AlSb
GaAs
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
1000/T °K

FIG. 10

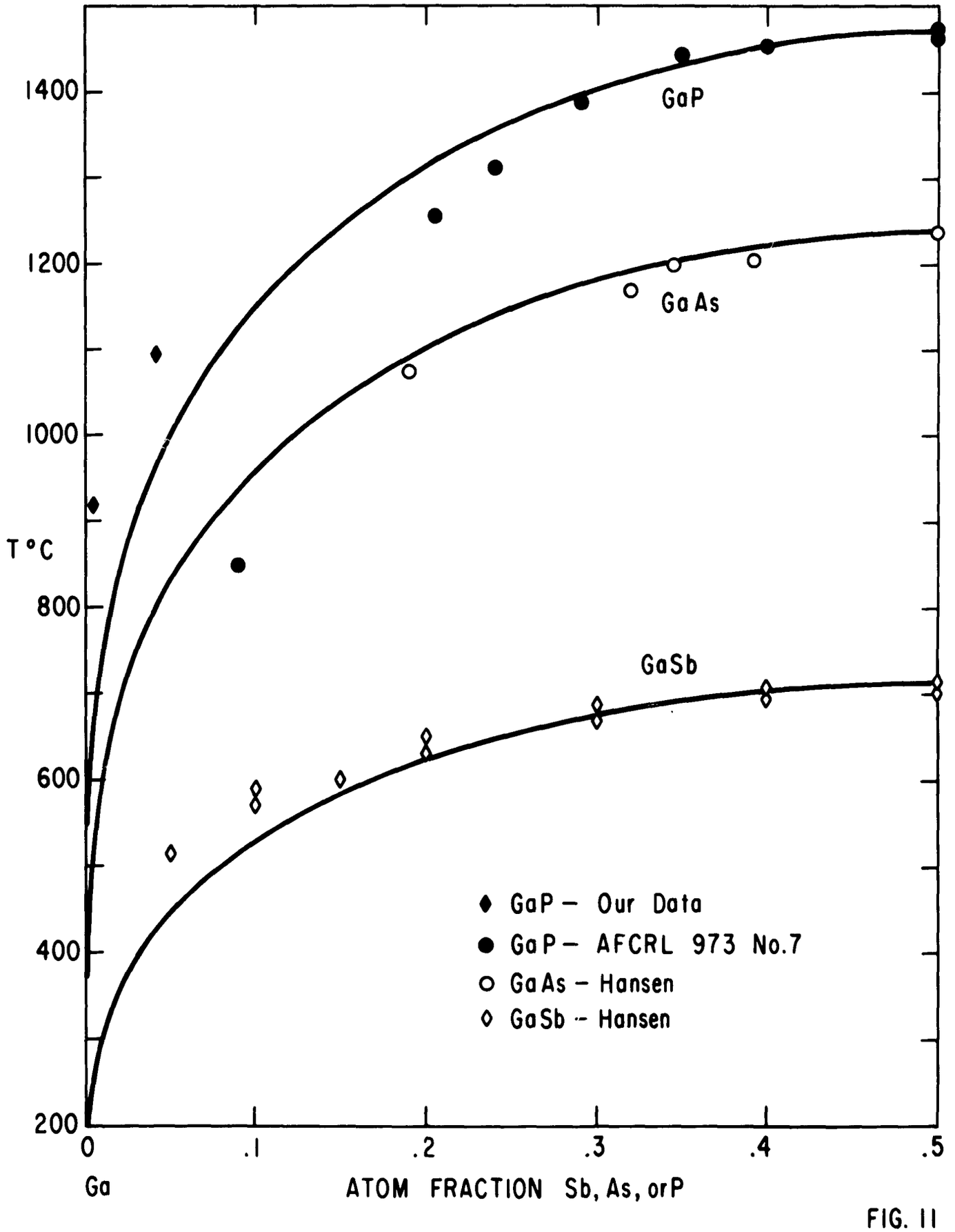
1400
1200
1000
800
600
400
200
T°C
GaP
GaAs
GaSb
GaP – Our Data
GaP – AFCRL 973 No.7
GaAs – Hansen
GaSb – Hansen
0
.1
.2
.3
.4
.5
Ga
ATOM FRACTION Sb, As, orP

FIG. 11

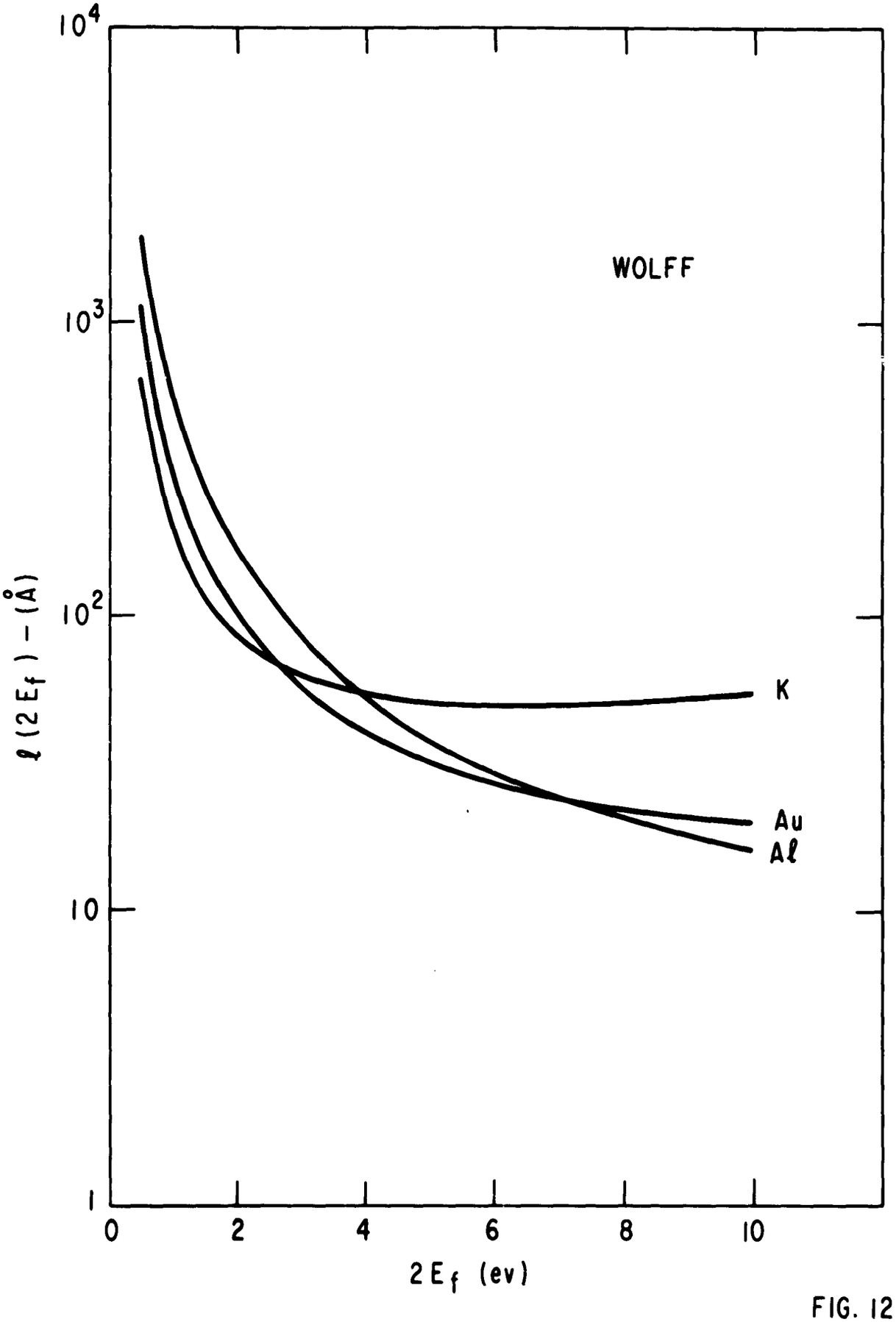

FIG. 12

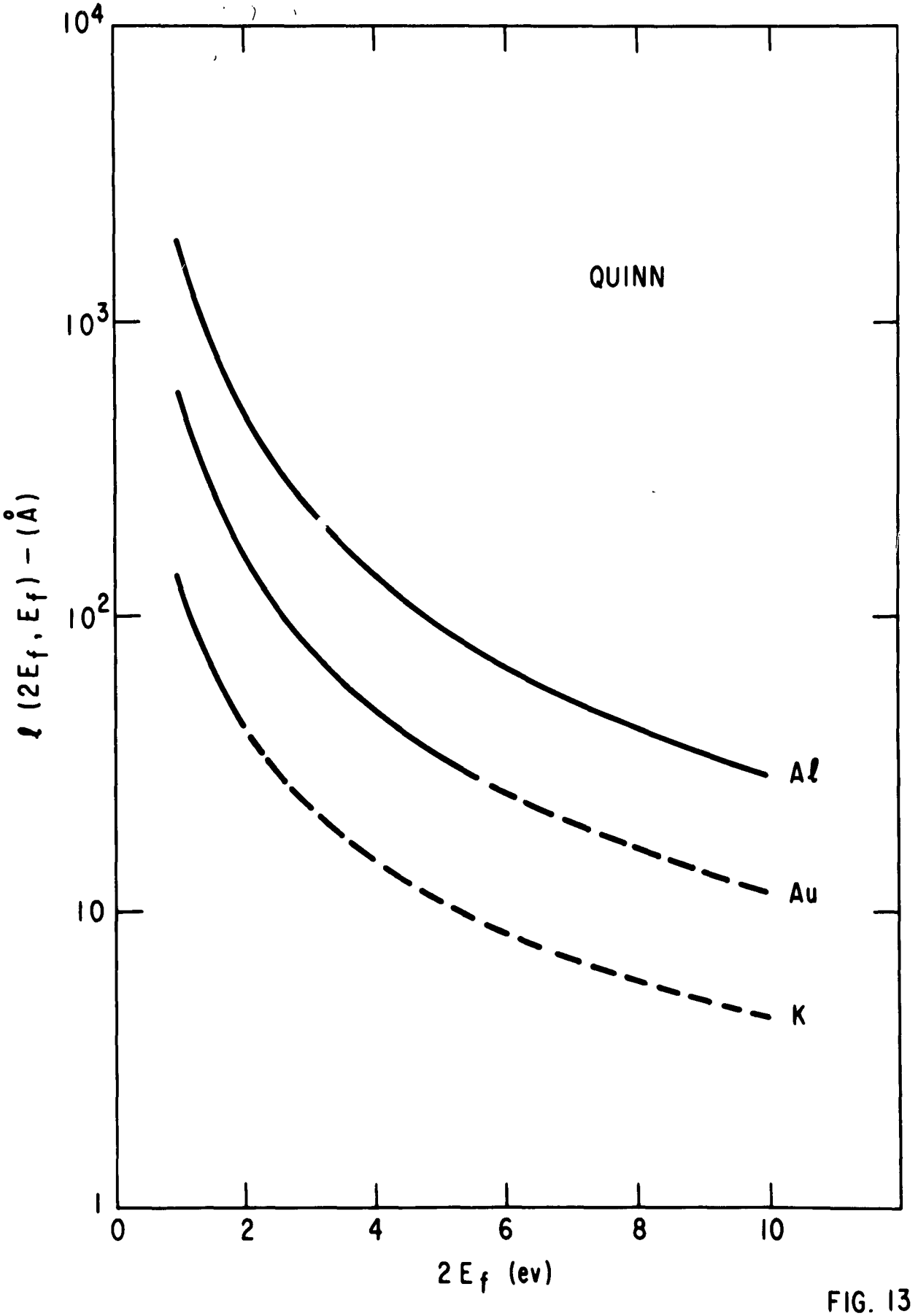
QUINN
10^4
10^3
10^2
10
1
$\ell\,(2E_f, E_f) - (\mathring{A})$
0
2
4
6
8
10
$2E_f$ (ev)
Al
Au
K

FIG. 13

CONTRIBUTORS

Scientists and technicians who contributed to the work reported:

Staff	Technicians
RN Hall	TJ Soltys
JH Racette	S Schwarz

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R. N. Hall, "Current Gain in Metal-Insulator Tunnel Triodes", Solid State Electronics, to be published.